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(54) HIGHLY CRYSTALLINE MN_2O_3 OR MN_3O_4 MANGANESE OXIDES

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(22) Filed: **Apr. 26, 2001**

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Related U.S. Application Data

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(60) Provisional application No. 60/104,396, filed on Oct. 15, 1998, and provisional application No. 60/105,088, filed on Oct. 21, 1998.

(51) **Int. Cl.**^{7} **C01G 45/02**
(52) **U.S. Cl.** **423/605**; 423/224; 423/599; 252/518.1
(58) **Field of Search** 423/599, 605; 429/224; 252/518.1

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(57) **ABSTRACT**

The present invention includes lithium manganese oxide spinel compounds having a low porosity, a high tap density and a high pellet density, and methods of preparing these compounds. In particular, the method comprises preparing a lithium manganese oxide with a spinel structure and having the formula: wherein:

$$Li_{1+X}Mn_{2-Y}M_{m_1}{}^1M_{m_2}{}^2 \ldots M_{m_k}{}^kO_{4+Z}$$

M^1, M^2, . . . M^k are cations different than lithium or manganese selected from the group consisting of alkaline earth metals, transition metals, B, Al, Si, Ga and Ge;

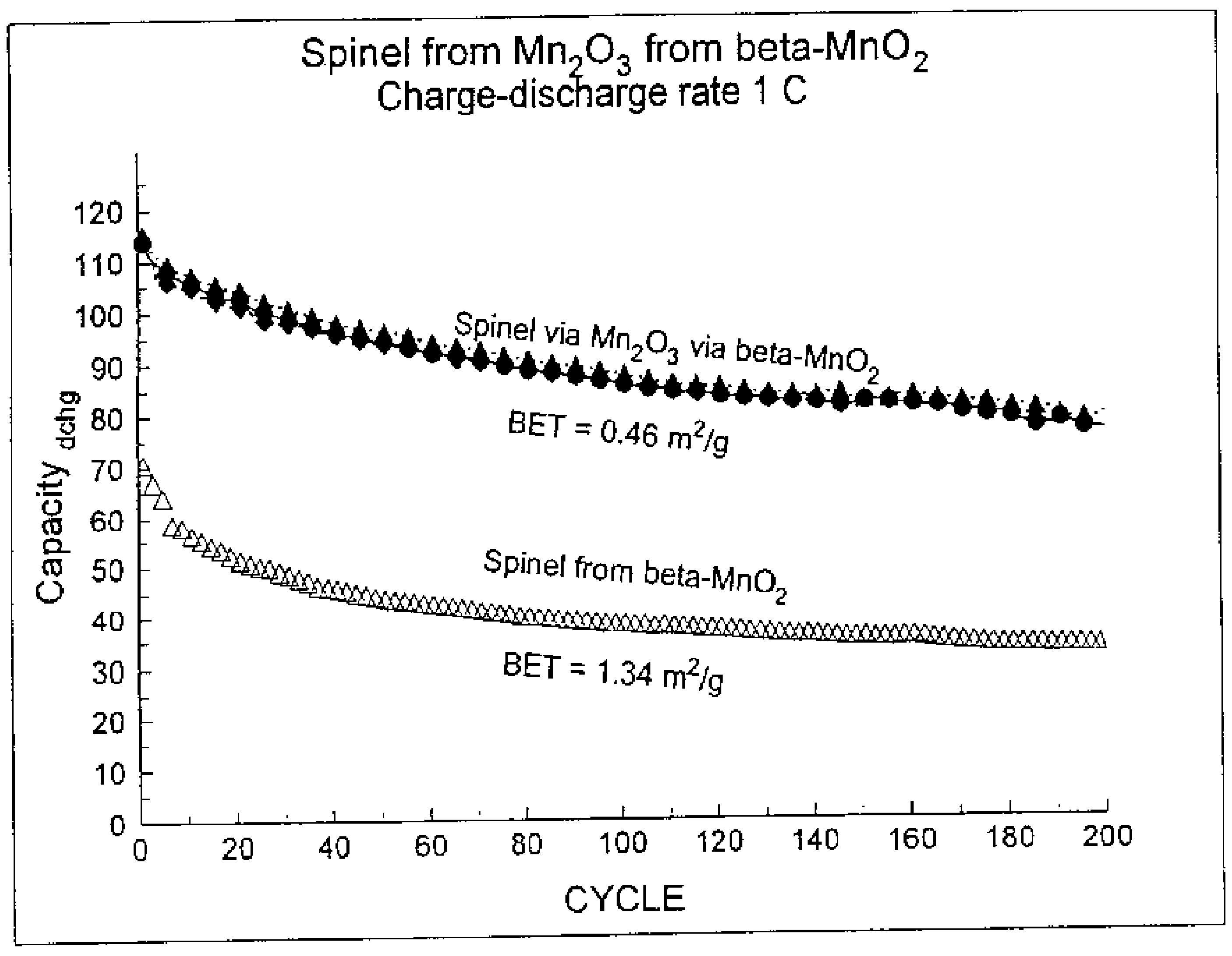
X, Y, m_1, m_2, . . . , m_k, each have a value between 0 and 0.2;

Z has a value between –0.1 and 0.2; and

X, Y, m_1, m_2, . . . m_k are selected to satisfy the equation:

$$Y=X+m_1+m_2+ \ldots +m_k.$$

11 Claims, 7 Drawing Sheets



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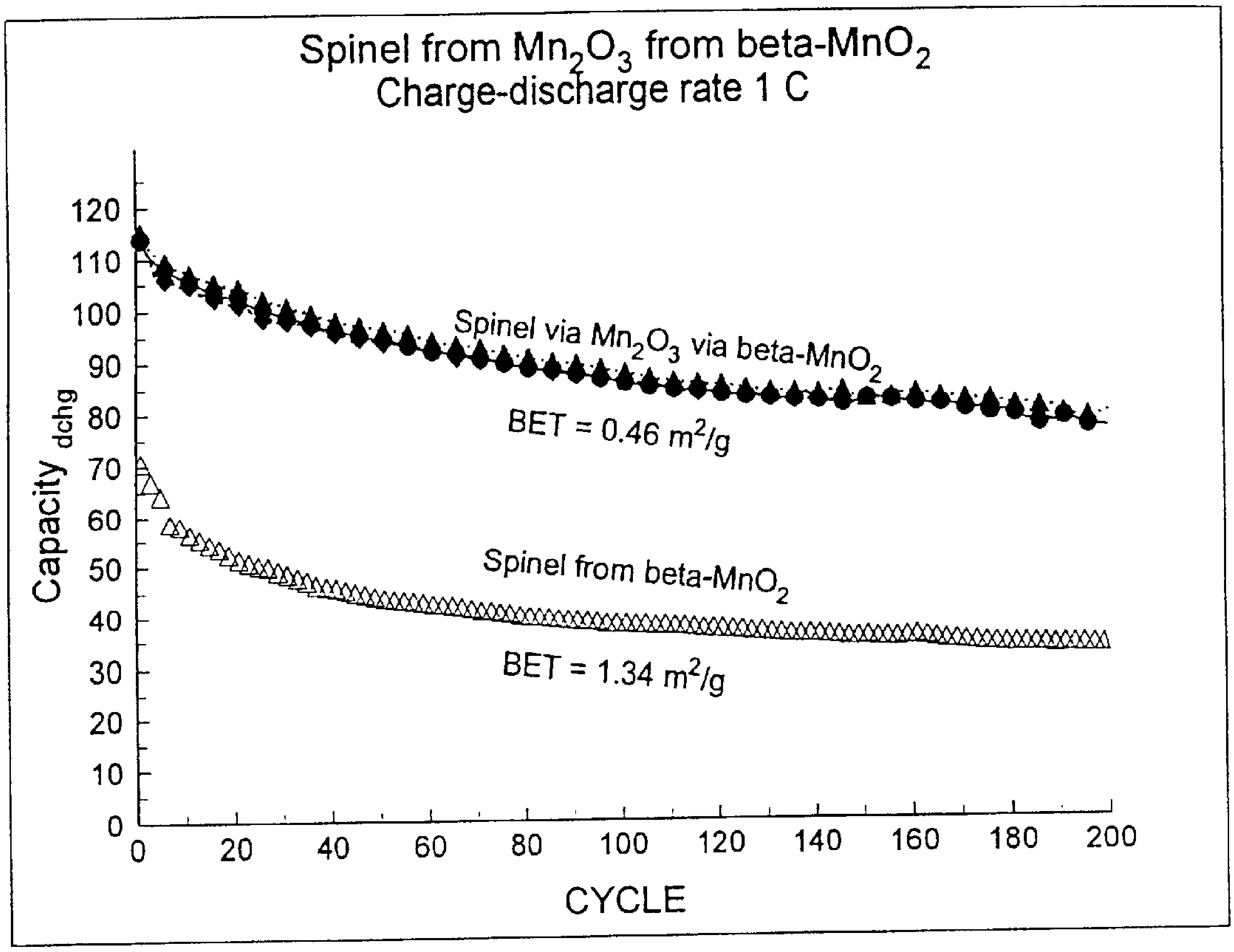
Spinel from Mn_2O_3 from beta-MnO_2
Charge-discharge rate 1 C
Capacity dchg
120
110
100
90
80
70
60
50
40
30
20
10
0
Spinel via Mn_2O_3 via beta-MnO_2
BET = 0.46 m^2/g
Spinel from beta-MnO_2
BET = 1.34 m^2/g
0
20
40
60
80
100
120
140
160
180
200
CYCLE

Fig. 1

$LiMn_2O_4$ from Mn_2O_3 via ß-MnO_2

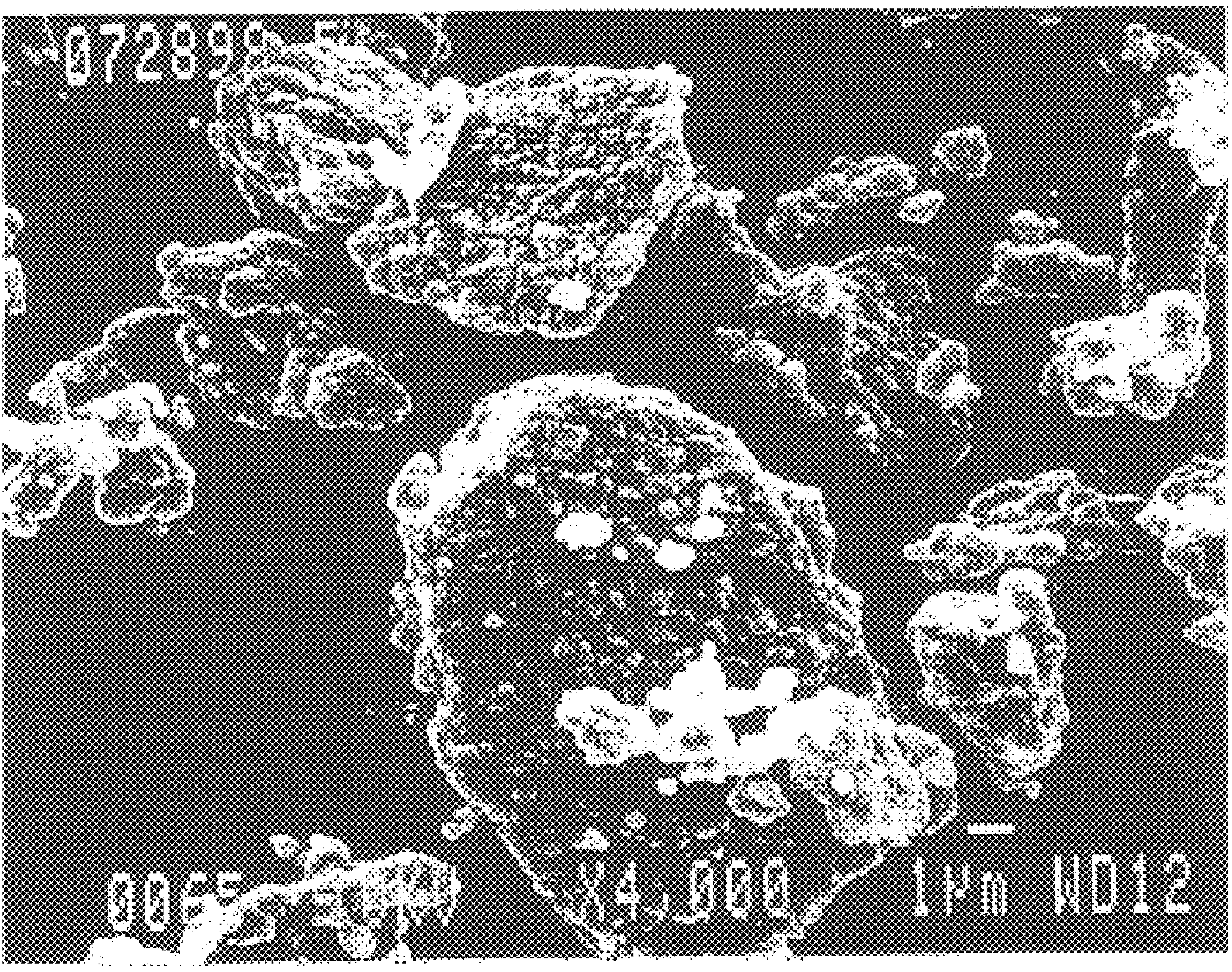

Fig. 2A X 4000

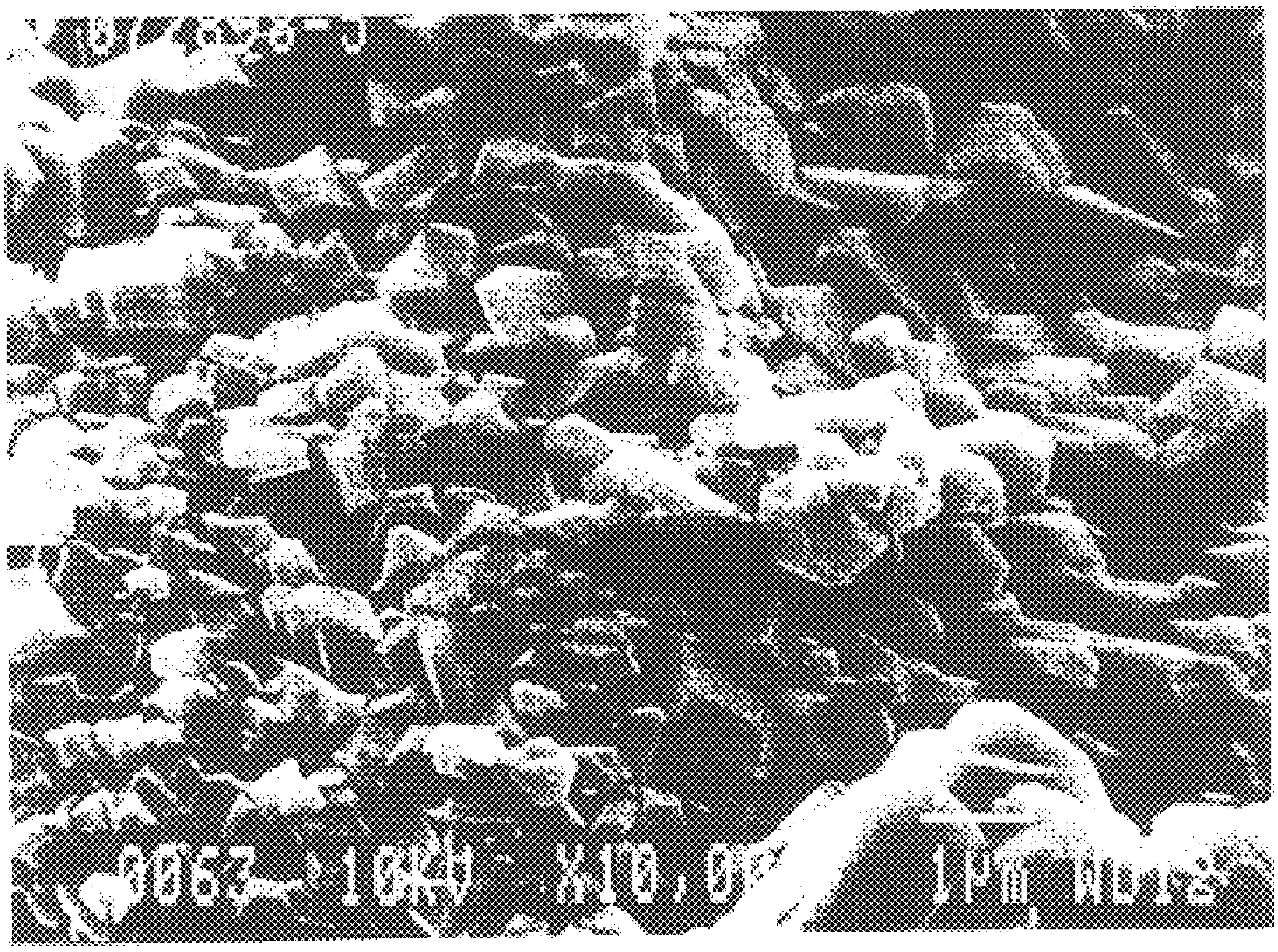

Fig. 2B X 10000

Fig. 2

$LiMn_2O_4$ from $MnCO_3$

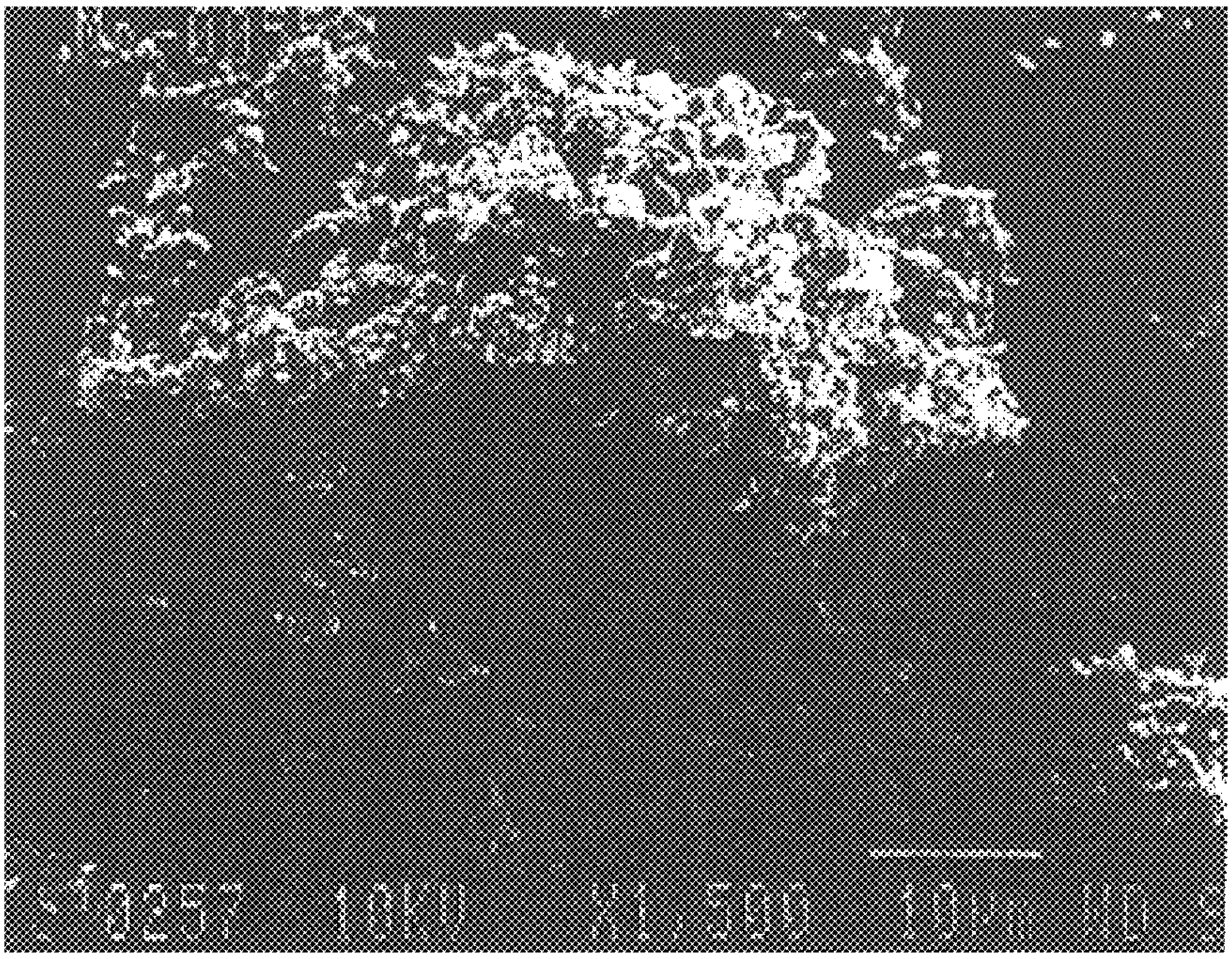

Fig.3A X 1500

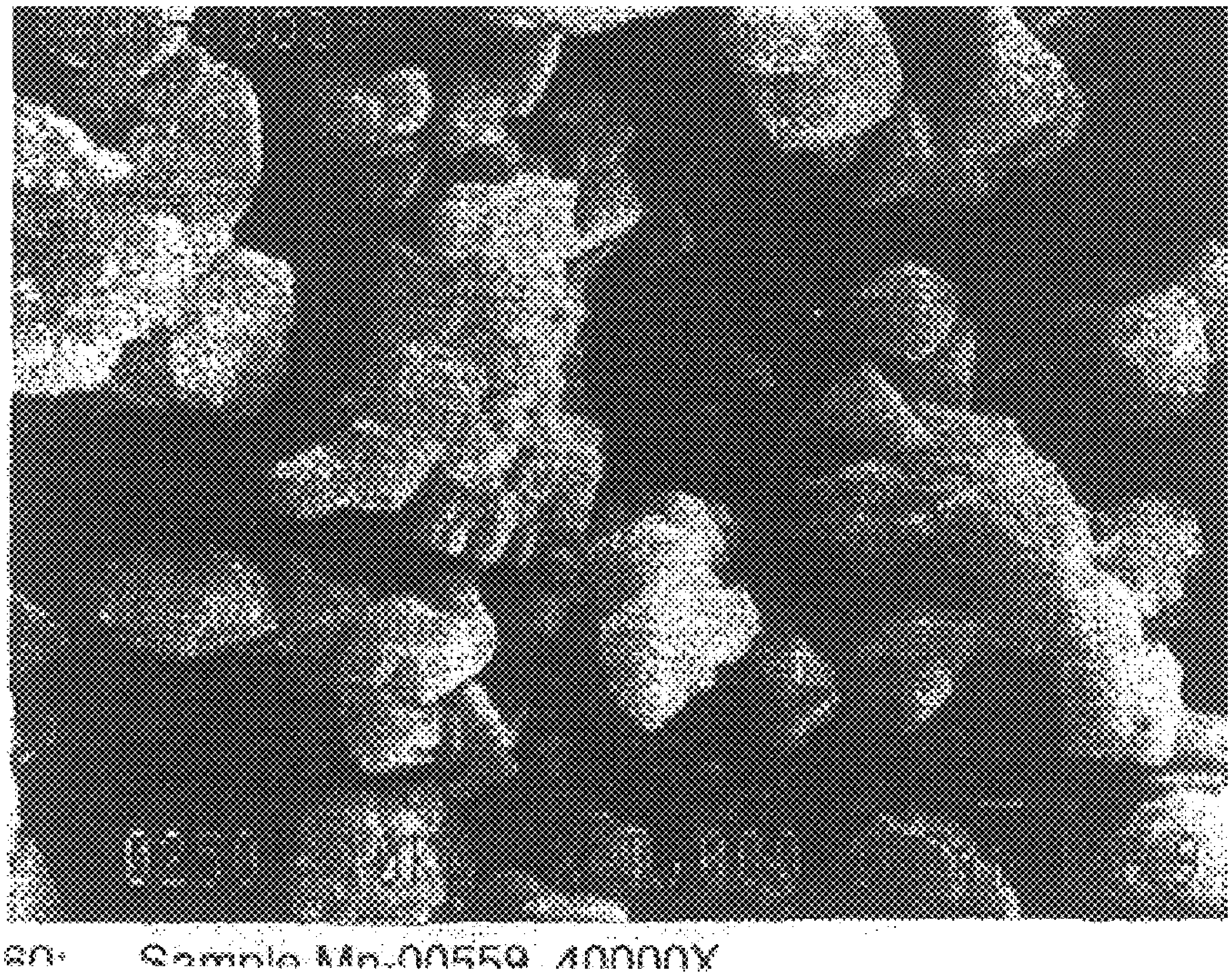

Fig.3B X 40000

Fig. 3

LiMn2O4 from γ-MnO_2 (EMD)

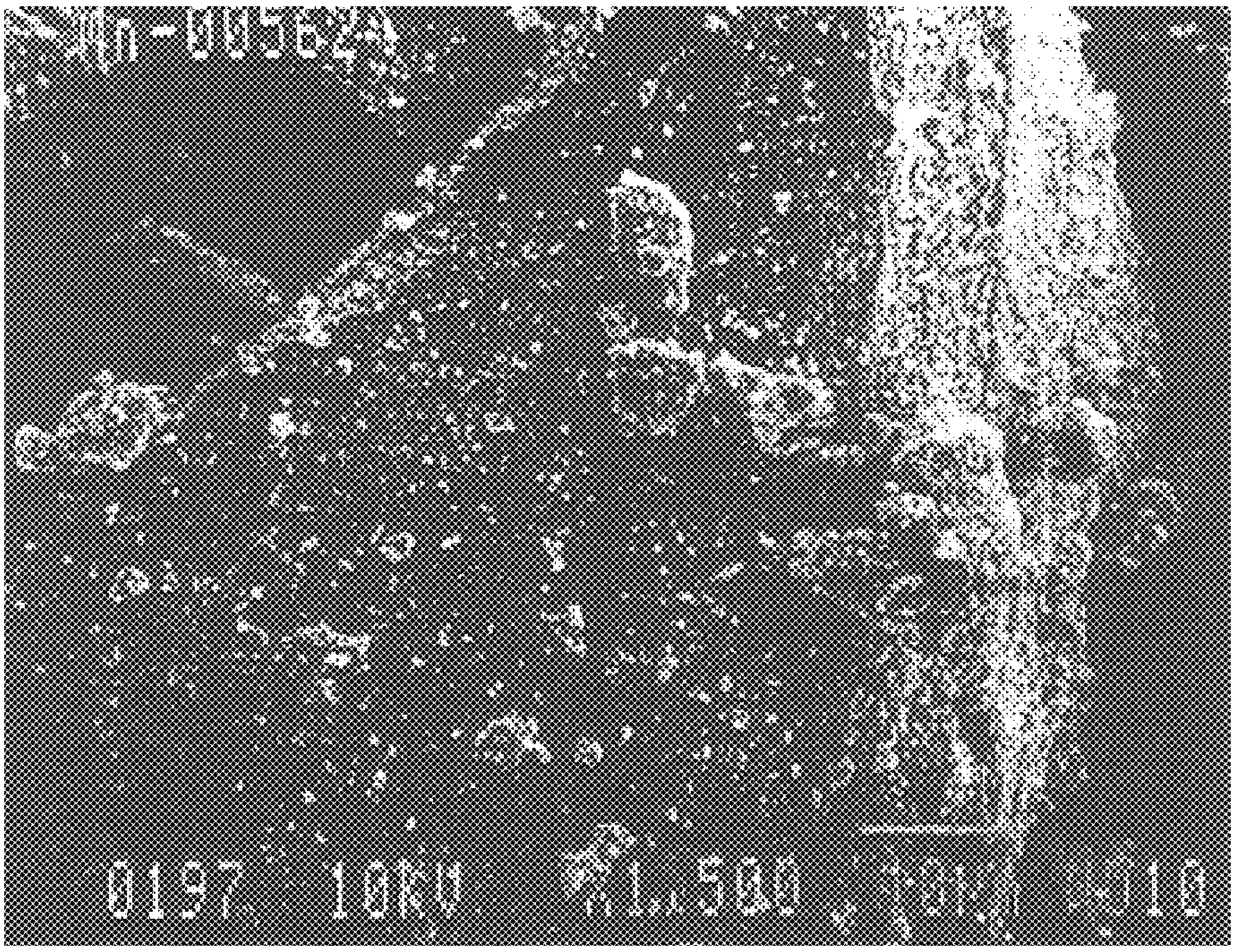

Fig. 4A X 1500

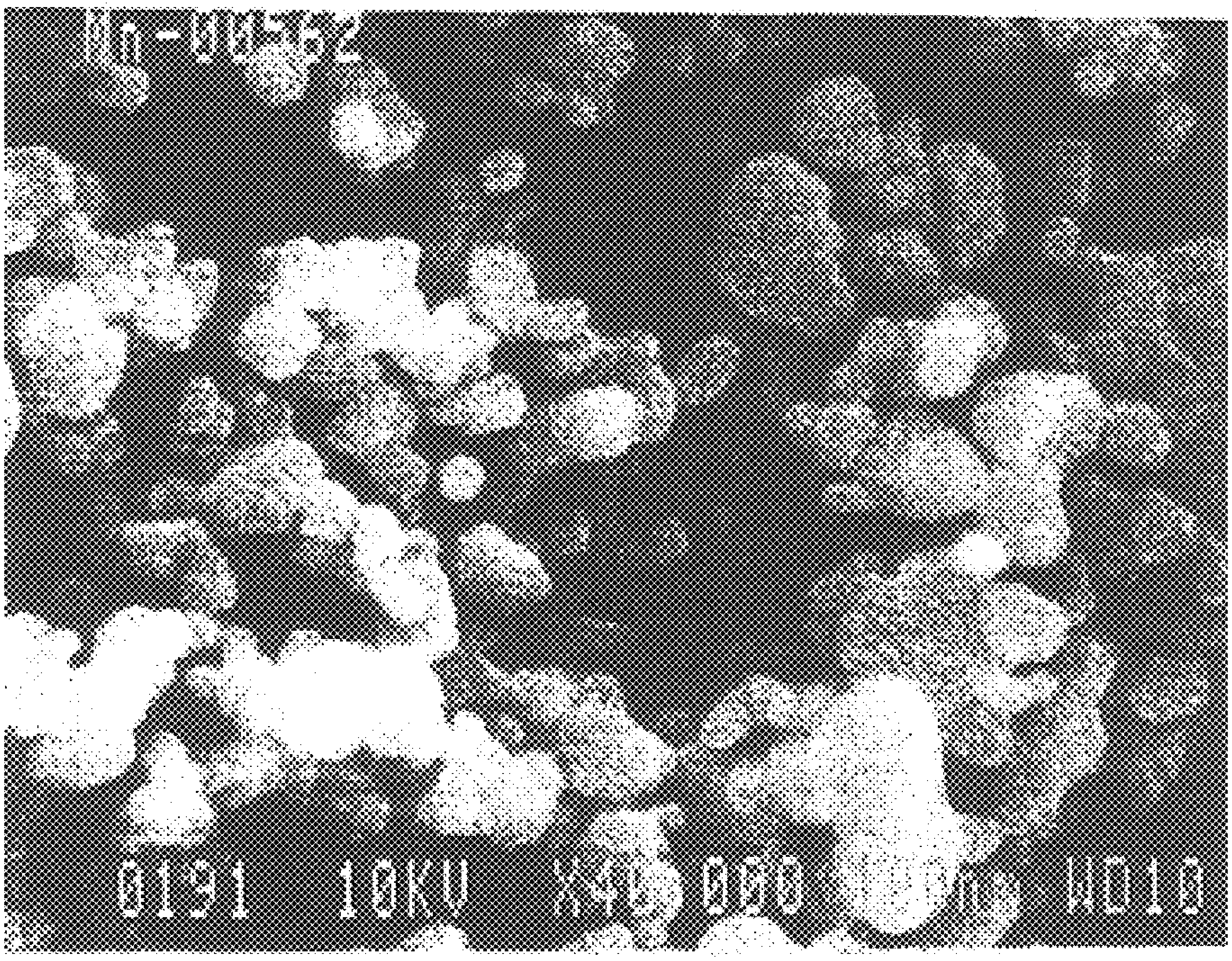

Fig. 4B X 40000

Fig. 4

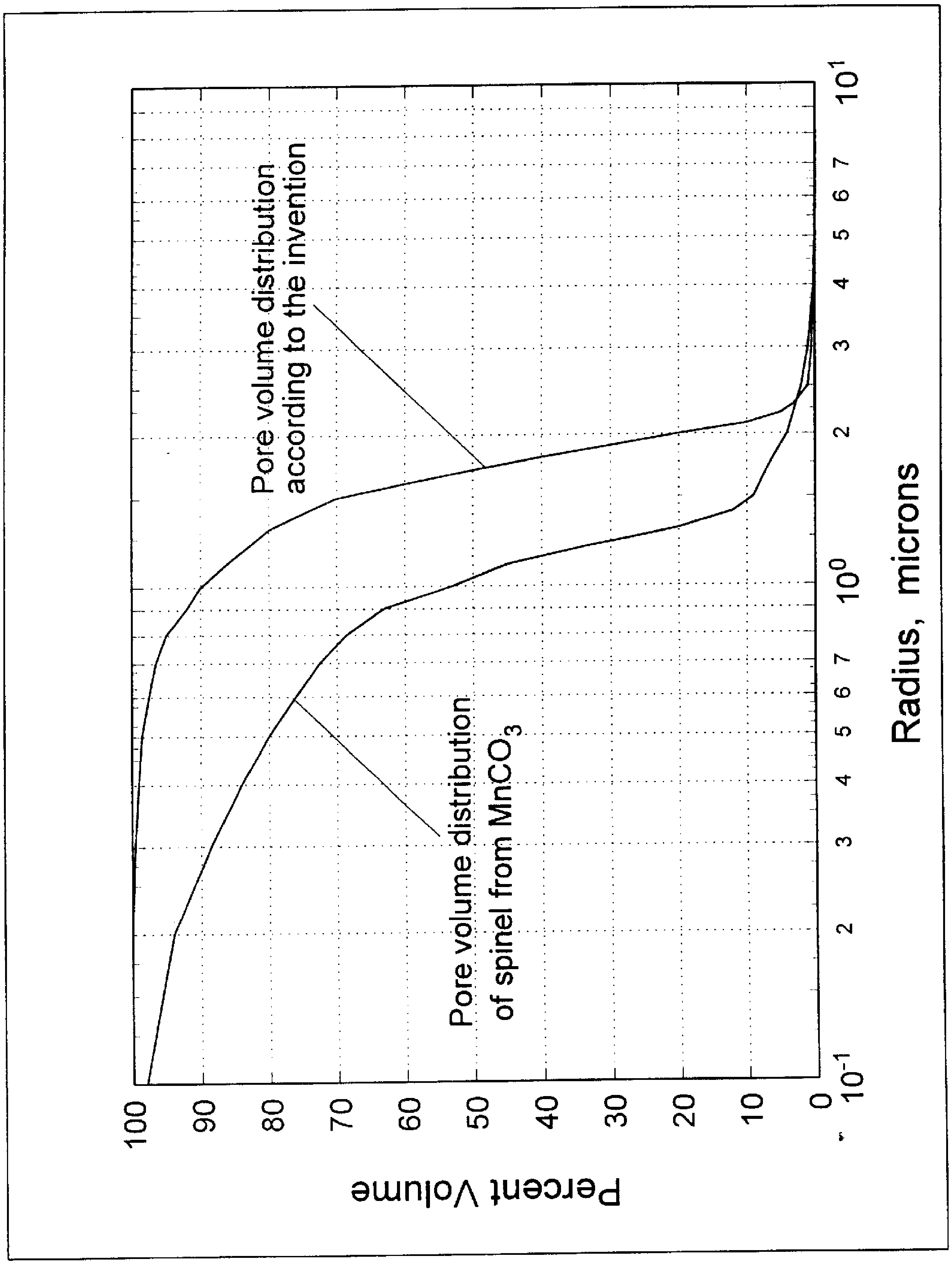
Pore volume distribution according to the invention
Pore volume distribution of spinel from $MnCO_3$
Percent Volume
0
10
20
30
40
50
60
70
80
90
100
Radius, microns
10^{-1}
2
3
4
5
6
7
10^{0}
2
3
4
5
6
7
10^{1}

Fig. 5

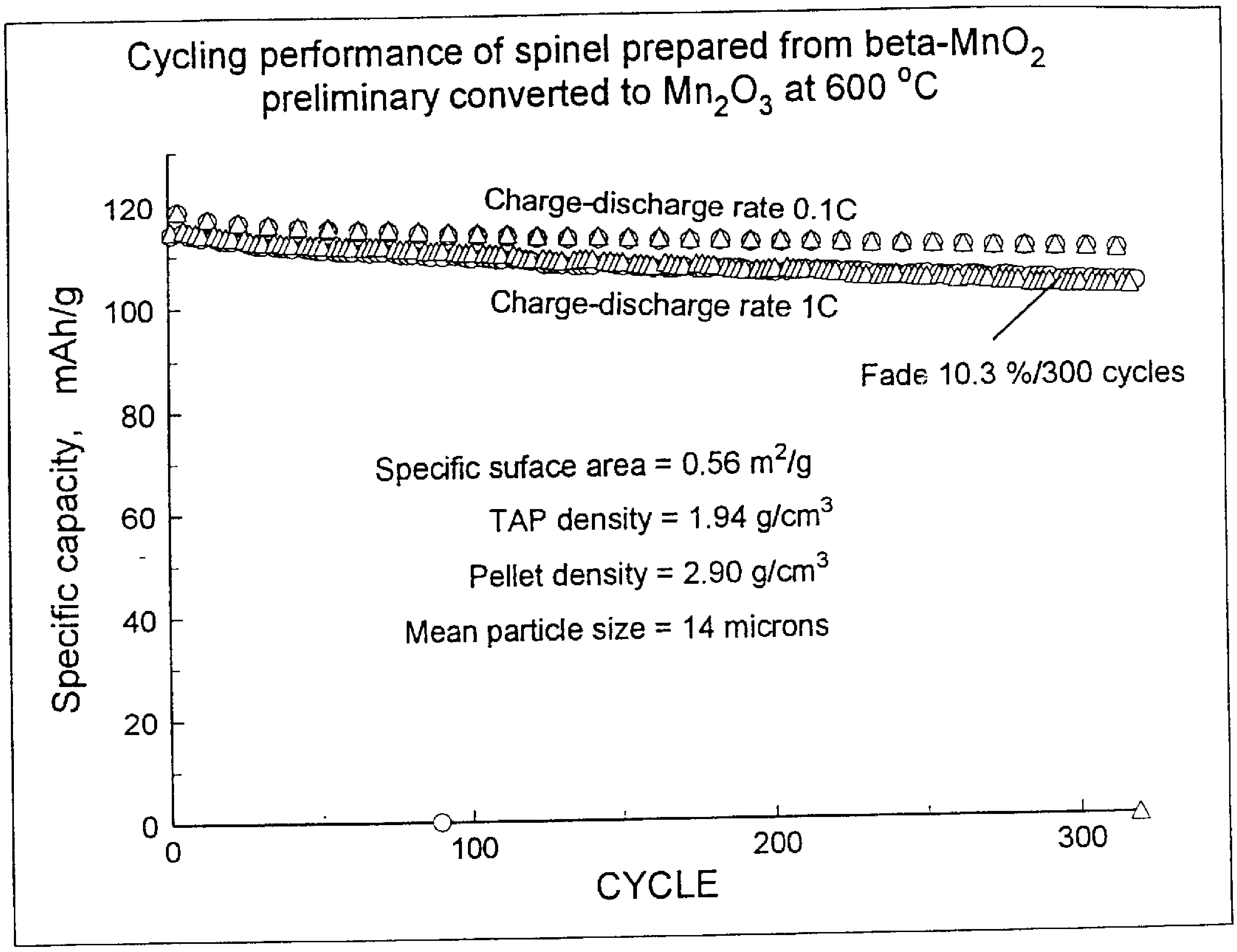
Cycling performance of spinel prepared from beta-MnO2 preliminary converted to Mn2O3 at 600 °C
Charge-discharge rate 0.1C
Charge-discharge rate 1C
Fade 10.3 %/300 cycles
Specific suface area = 0.56 m2/g
TAP density = 1.94 g/cm3
Pellet density = 2.90 g/cm3
Mean particle size = 14 microns
Specific capacity, mAh/g
120
100
80
60
40
20
0
0
100
200
300
CYCLE

Fig. 6

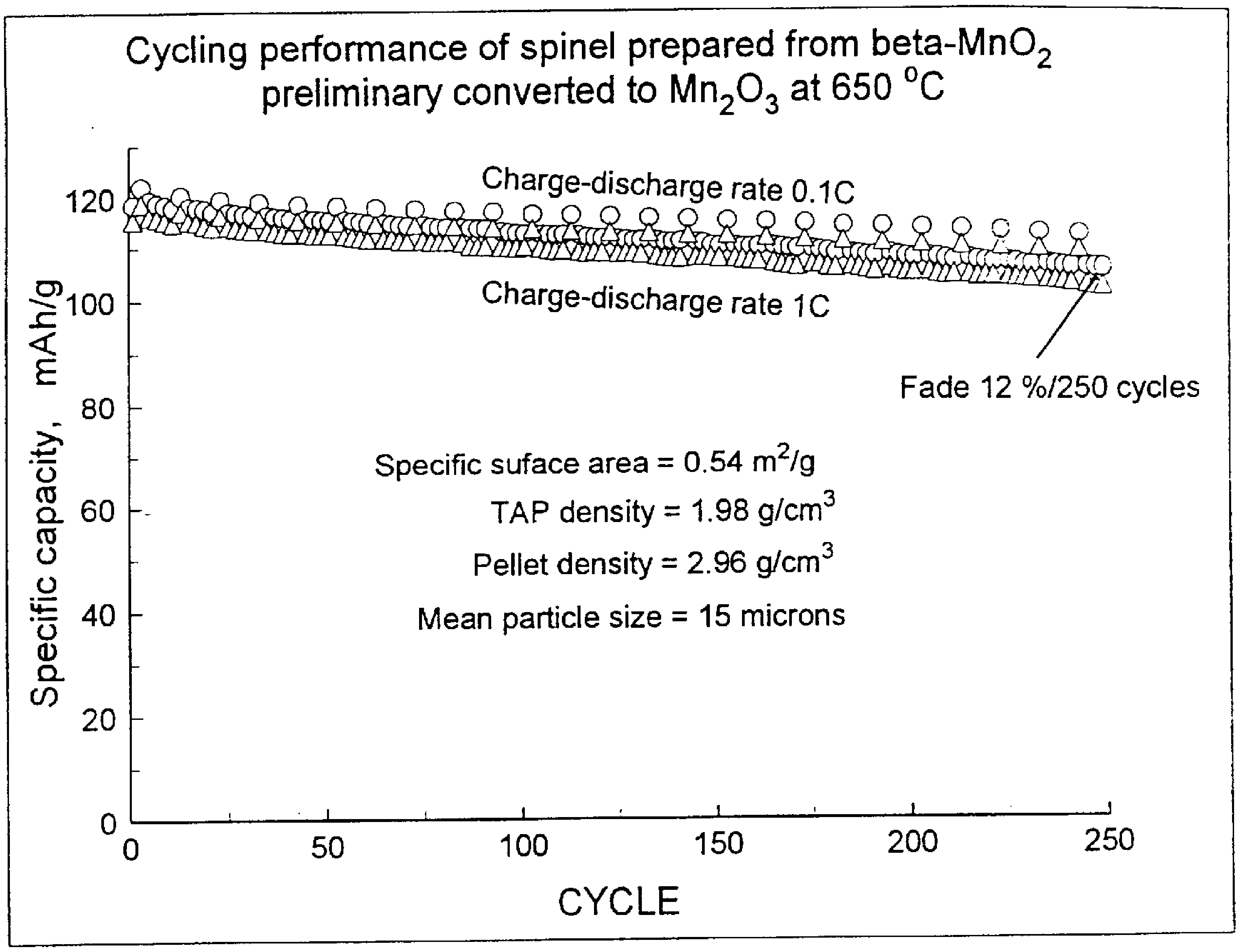
Cycling performance of spinel prepared from beta-MnO_2 preliminary converted to Mn_2O_3 at 650 °C
Charge-discharge rate 0.1C
Charge-discharge rate 1C
Fade 12 %/250 cycles
Specific suface area = 0.54 m^2/g
TAP density = 1.98 g/cm^3
Pellet density = 2.96 g/cm^3
Mean particle size = 15 microns
Specific capacity, mAh/g
0
20
40
60
80
100
120
CYCLE
0
50
100
150
200
250

Fig. 7

HIGHLY CRYSTALLINE MN_2O_3 OR MN_3O_4 MANGANESE OXIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of U.S. patent application Ser. No. 09/418,352, filed Oct. 14, 1999, now U.S. Pat. No. 6,267,943 which claims the benefit of U.S. Provisional Application Serial No. 60/104,396, filed Oct. 15, 1998, and U.S. Provisional Application Serial No. 60/105,088, filed Oct. 21, 1998, under 35 U.S.C. §119(e).

FIELD OF THE INVENTION

This invention relates to lithiated metal oxide intercalation compounds, and particularly to lithium manganese oxides with spinel structures for positive electrodes in 4 V secondary lithium and lithium-ion batteries.

BACKGROUND OF THE INVENTION

Lithium manganese oxide spinel compounds such as $Li_{1+X}Mn_{2-X}O_{4+Y}$ have been used as positive electrode material for 4 V secondary lithium and lithium-ion batteries. Typically, these spinel compounds are formed by firing (calcining) a mixture of a manganese source compound and a lithium source compound. Exemplary manganese source compounds include manganese carbonate ($MnCO_3$), electrochemical manganese dioxide (γ-MnO_2 or EMD), and chemical manganese dioxide (γ-NnO_2 or CMD).

As described in coassigned U.S. Pat. No. 5,789,115, the mean particle size and particle size distribution of these compounds and, in particular, $Li_{1+X}Mn_{2-X}O_{4+Y}$, is dependent on the mean particle size and particle size distribution of the raw materials used to make these compounds and specifically the manganese source compound. In addition to affecting the particle size and particle size distribution of the lithium manganese oxide, the morphology, e.g., density and porosity, of the manganese source compound can affect the morphology of the resulting lithium manganese oxides. In particular, the crystal growth of the spinel phase using a low density manganese compound causes an increase in the distance between the spinel crystallites and has a negative effect on the final density of the spinel compound. This presents a problem with $MnCO_3$ and CMD because these manganese source compounds have relatively low densities and thus produce a low density product. Because EMD has a higher density than $MnCO_3$ and CMD, EMD is often used instead of these manganese source compounds to produce spinel compounds. Nevertheless, the combined water, porosity and vacancies in the EMD structure have a negative effect on the density of the resulting spinel compound.

The morphology of the manganese source compound also affects the tap and pellet density of the spinel compound. The tap and pellet density are important properties characterizing positive electrode materials for secondary lithium and lithium-ion batteries. In particular, these properties directly influence the specific cell energy, cell safety performance, manganese dissolution, capacity fade and capacity loss at room and elevated temperatures, for the electrochemical cell. Therefore, providing a method for preparing lithium manganese oxide spinel compounds having a desired tap and pellet density is of great importance in developing high energy density and high electrochemical performance 4 V secondary lithium and lithium ion batteries.

SUMMARY OF THE INVENTION

The present invention is directed to lithium manganese oxide spinel compounds having a low porosity, a high tap density and a high pellet density, and a method of preparing these compounds. In particular, the method comprises preparing a lithium manganese oxide with a spinel structure and having the formula:

$$Li_{1+X}Mn_{2-Y}M_{m_1}^{1}M_{m_2}^{2}\ldots M_{m_k}^{k}O_{4+Z}$$

wherein:

- M^1, M^2, . . . M^k are cations different than lithium or manganese selected from the group consisting of alkaline earth metals, transition metals, B, Al, Si, Ga and Ge;
- X, Y, m_1, m_2, . . . m_k are molar parts, each having a value between 0 and 0.2;
- Z is a molar part having a value between −0.1 and 0.2; and
- the molar parts X, Y, m_1, m_2, . . . m_k are selected to satisfy the equation:

$$Y=X+m_1+m_2+\ldots+m_k$$

These lithium manganese oxide compounds are produced by calcining a mixture comprising at least one manganese oxide (manganese source compound) selected from the group consisting of Mn_2O_3 or Mn_3O_4, at least one lithium compound, and optionally at least one M^1, M^2, . . . M^k source compound, in at least one firing step at a temperature between about 400° C. and about 900° C.

The manganese oxide compounds can be formed by firing highly crystalline β-MnO_2 at a temperature between about 500° C. and 1000° C. Preferably, the β-MnO_2 is fired at a temperature between about 600° C. and about 800° C. in the preparing step to form Mn_2O_3 manganese oxide. The highly crystalline β-MnO_2 used to produce the Mn_2O_3 or Mn_3O_4 is preferably formed by firing $Mn(NO_3)_2$ at a temperature between about 200° C. and about 400° C. to thermally decompose the $Mn(NO_3)_2$ and form β-MnO_2. In addition, the β-MnO_2 preferably has a mean particle size of between about 5 μm and about 20 μm and can be ground to produce this mean particle size.

In the calcining step, the mixture of source compounds is fired at between about 400° C. and about 900° C. Preferably, the mixture is calcined using more than one firing step at firing temperatures within this temperature range. During calcination, agglomeration of the spinel particles is preferably prevented. For example, during a multiple step firing sequence, agglomeration can be prevented by firing the source compounds in a fluid bed furnace or rotary calciner during at least a portion of the firing steps or by grinding the spinel material between steps. The lithium manganese oxide spinel compounds of the invention can be used as positive electrode material for a secondary lithium or lithium-ion electrochemical cell.

The lithium manganese oxide spinel compounds of the invention have a high tap density and pellet density and a low porosity and specific area. In addition, these compounds have a high specific capacity, low capacity fade during cycling, and a low capacity loss during storage at room and elevated temperatures. In particular, the spinel compounds of the invention have a tap density of greater than 1.9 g/cm^3 and preferably greater than 2.1 g/cm^3. The pellet density for those spinel compounds is greater than 2.85 g/cm^3, preferably greater than 2.90 g/cm^3, or even greater than 2.95 g/cm^3. The pore volume of the pores having a mean radius of less than 1 micron in the spinel compound is no more than 20%, preferably no more than 15% or even no more than 10%, of the total pore volume of the spinel compound, thus illustrating the low porosity of the spinel compound. In addition, the specific area of the spinel compound is less than about 0.8 m^2/g and preferably less than 0.6 m^2/g or even less than 0.5 m^2/g.

The present invention also includes the Mn_2O_3 and Mn_3O_4 manganese oxide compounds used to produce the spinel compounds of the invention. These manganese oxide compounds are highly crystalline and have a low porosity. In particular, these manganese oxide compounds have a porosity such that the pore volume of pores having a mean radius of less than 1 micron in said manganese oxide is no more than 20% of the total pore volume of said manganese oxide. These manganese oxides also have a specific area of less than 2.0 m^2/g, preferably less than 1.5 m^2/g or even less than 1.0 m^2/g. The tap density of the manganese oxides is preferably greater than 2.2 g/cm^3, more preferably greater than 2.4 g/cm^3.

These and other features and advantages of the present invention will become more readily apparent to those skilled in the art upon consideration of the following detailed description and accompanying drawings which describe both the preferred and alternative embodiments of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

This invention may be better understood and its numerous objects and advantages will become apparent to those skilled in the art by reference to the accompanying drawings and photographs as follows:

FIG. **1** is a graph of specific capacity v. charge-discharge cycles for $Li_{1.04}Mn_{1.96}O_4$ spinel compounds and compares the specific capacity and cycleability of spinel compounds prepared directly from β-MnO_2 and prepared according to the present invention using a Mn_2O_3 precursor obtained from β-MnO_2.

FIGS. **2**A and **2**B are SEM photographs of lithium manganese oxide spinel compounds prepared from a Mn_2O_3 precursor obtained from β-MnO_2 according to the present invention and demonstrating the dense structure of the spinel compounds of the invention.

FIGS. **3**A and **3**B are scanning electron microscope (SEM) photographs of a spinel compound prepared from $MnCO_3$ by calcination at 825° C.

FIGS. **4**A and **4**B are SEM photographs of a spinel compound prepared from γ-MnO_2 (EMD) by calcination at 750° C.

FIG. **5** is a graph illustrating the integral porosity as a function of pore radius of spinel compounds of the invention compared to the integral porosity of spinel compounds produced from $MnCO_3$.

FIG. **6** is a graph of specific capacity v. charge-discharge cycles illustrating the cycling performance (i.e. specific capacity and cycleability) at 1 hour and 10 hour charge-discharge rates for $Li_{1.03}Mn_{1.96}Co_{0.01}O_4$ spinel compounds prepared according to the present invention from a Mn_2O_3 precursor converted from β-MnO_2 at 600° C.

FIG. **7** is a graph of specific capacity v. charge-discharge cycles illustrating the cycling performance (i.e. specific capacity and cycleability) at 1 hour and 10 hour charge-discharge rates for $Li_{1.03}Mn_{1.96}Co_{0.01}O_4$ spinel compounds prepared according to the present invention from a Mn_2O_3 precursor converted from β-MnO_2 at 650° C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be understood by those skilled in the art in reading this application, the term "lithium manganese oxide" includes not only compounds that include only lithium, manganese and oxygen, but also compounds that include dopants such as alkaline earth metals, transition metals, B, Al, Si, Ga and Ge.

It has been unexpectedly discovered in accordance with the invention that using Mn_2O_3 or Mn_3O_4, preferably formed from β-MnO_2, to produce lithium manganese oxide spinel compounds can produce spinel compounds having good electrochemical performance and excellent pellet and tap densities. In particular, β-MnO_2, Mn_2O_3, and Mn_3O_4 are known in the art as being chemically inactive with lithium salts. For example, as shown in FIG. **1**, lithium manganese oxide spinels formed directly from β-MnO_2 have extremely poor electrochemical performance. However, it has been discovered that by using highly crystalline Mn_2O_3 or Mn_3O_4 prepared, e.g., using highly crystalline β-MnO_2, a high density manganese oxide can be obtained having a high chemical activity. The highly crystalline β-MnO_2 used in the invention is not porous and thus has a greater density than $MnCO_3$, CMD and EMD. Furthermore, the β-MnO_2 has no combined water and has a highly ordered structure. Therefore, as shown in FIG. **1**, using β-MnO_2 to form a manganese precursor for lithium manganese oxide preparation leads to a product with dramatically better electrochemical performance than using β-MnO_2 directly.

As stated above, the β-MnO_2 preferably used to prepare the Mn_2O_3 and Mn_3O_4 manganese oxides is a highly crystalline β-MnO_2. The high crystallinity of the β-MnO_2 can be determined by measuring peak-widths using x-ray diffraction. An exemplary highly crystalline β-MnO_2 can be formed by firing $Mn(NO_3)_2$ at a temperature between about 200° C. and about 400° C. to thermally decompose the $Mn(NO_3)_2$ and form β-MnO_2. The β-MnO_2 is fired at a temperature between about 500° C. and about 1000° C. to produce Mn_2O_3 or Mn_3O_4. Preferably, the β-MnO_2 is fired at a temperature between about 600° C. and about 800° C. to form Mn_2O_3. In addition, the β-MnO_2 is preferably fired for between about 1 hour and 10 hours to produce these manganese oxides but can be fired for a longer period of time without negative effects. The β-MnO_2 preferably has a mean particle size of between about 5 μm and 20 μm prior to forming the manganese oxides and can be ground to this mean particle size prior to firing.

In one embodiment of the invention, the β-MnO_2 is fired at a starting temperature of about 500° C. and the temperature slowly raised (e.g. at a rate of less than about 1° C./min) to a final temperature between about 600° C. and about 650° C. to thermally decompose the β-MnO_2 to form Mn_2O_3. By slowly raising the temperature, a Mn_2O_3 compound with an even better density and chemical activity is obtained.

The Mn_2O_3 or Mn_3O_4 manganese oxides resulting from firing β-MnO_2 have a tap density of greater than 2.2 g/cm^3, and preferably greater than 2.4 g/cm^3. In addition, the particle size of the Mn_2O_3 or Mn_3O_4 is typically between about 1.1 and 1.3 times the size of the β-MnO_2, i.e., between about 6 μm and 25 μm. The specific area of the Mn_2O_3 or Mn_3O_4 is less than 2.0 m^2/g and preferably less than 1.5 m^2/g, or even less than 1.0 m^2/g (as determined by one point BET). These manganese oxides also preferably have high crystallinity and low porosity. In particular, the porosity of these manganese oxides is preferably such that the pore volume of the pores having a mean radius of less than 1 micron is no more than 20%, preferably no more than 15% or even no more than 10% of the total pore volume of the manganese oxide using Mercury porosimetry. In addition to using highly crystalline Mn_2O_3 or Mn_3O_4 formed from β-MnO_2, highly crystalline Mn_2O_3 or Mn_3O_4 prepared by other methods and having the above properties can also be used in the present invention.

The Mn_2O_3 or Mn_3O_4 is combined with lithium source compounds and optionally dopant ($M^1, M^2, \ldots M^k$) source compounds to produce a stoichiometric mixture according to the formula:

$$Li_{1+X}Mn_{2-Y}M_{m_1}^{1}M_{m_2}^{2} \ldots M_{m_k}^{k}O_{4+Z}$$

wherein:

- $M^1, M^2, \ldots M^k$ are cations different than lithium or manganese selected from the group consisting of alkaline earth metals, transition metals, B, Al, Si, Ga and Ge;
- $X, Y, m_1, m_2, \ldots m_k$ are molar parts, each having a value between 0 and 0.2;
- Z is a molar part having a value between −0.1 and 0.2; and
- the molar parts $X, Y, m_1, m_2, \ldots m_k$ are selected to satisfy the equation:

$$Y=X+m_1+m_2+ \ldots +m_k$$

The lithium and dopant source compounds can be pure elements but are typically compounds containing the elements such as oxides or salts thereof. In addition, the lithium and dopant cations can each be supplied from separate source compounds or two or more of the cations can be supplied from the same source compounds. Preferably, the lithium source compounds include one or any combination of the following: LiOH, $LiNO_3$, Li_2CO_3, LiCl and LiF. The manganese oxide and lithium and dopant source compounds can be mixed in any desirable order. In addition, although the spinel compounds are preferably prepared by solid state reactions, it can be advantageous to react the raw materials using wet chemistry alone or in combination with solid state reactions. For example, the reaction mixture can be prepared by suspending source compounds in a solution of other source compounds and spray drying the resulting slurry to obtain an intimate mixture.

The mixture of the manganese oxide and lithium and dopant source compounds can be calcined in a solid state reaction to form a lithium manganese oxide with a spinel structure by firing the mixture in at least one firing step at a temperature between about 400° C. and about 900° C. in the presence of oxygen, e.g., in an atmosphere having an oxygen partial pressure of at least 10 kpa. Exemplary firing sequences are disclosed, e.g., in coassigned U.S. Pat. Nos. 5,718,877 and 5,792,442. Preferably, the mixture is calcined using more than one firing step at firing temperatures between about 450° C. and 850° C. and for a total firing time between about 4 and about 48 hours to form the spinel compounds. The mixture can also be fired for a longer period of time without negatively affecting the resulting product. Once the mixture has been fired to form the lithium manganese oxide spinel compound, the resulting compound is preferably cooled to ambient temperature in a controlled manner, e.g., at a rate of 1° C./min or less.

It has been discovered that agglomeration of the spinel particles occurs during spinel phase nucleation in the calcination step, e.g., during the initial firing step of a multiple step firing sequence. This agglomeration is preferably prevented by suitable means to produce spinel particles having a mean particle size between about 7 μm and about 30 μm. For example, agglomeration can be prevented by firing the mixture during at least the initial firing steps in a fluid bed furnace or rotary calciner to minimize the contact between the particles in the mixture. The spinel particles can also be ground to the desired particle size between firing steps, especially between the initial firing steps, to prevent agglomeration.

The resulting lithium manganese oxide spinel compounds have high tap and pellet densities. Preferably, these tap and pellet densities can be improved by mildly dispersing the resulting lithium manganese oxide spinel compounds in an unreactive solvent such as acetone. Alternatively, the spinel compound can be dispersed in a dry mixture by placing the compound in a mixer for a short period of time, e.g., 1 to 60 minutes.

The present invention also includes a lithium manganese oxide spinel compound having the formula:

$$Li_{1+X}Mn_{2-Y}M_{m_1}^{1}M_{m_2}^{2} \ldots M_{m_k}^{k}O_{4+Z}$$

wherein:

- $M^1, M^2, \ldots M^k$ are cations different than lithium or manganese selected from the group consisting of alkaline earth metals, transition metals, B, Al, Si, Ga and Ge;
- $X, Y, m_1, m_2, \ldots m_k$ are molar parts, each having a value between 0 and 0.2;
- Z is a molar part having a value between −0.1 and 0.2; and
- the molar parts $X, Y, m_1, m_2, \ldots m_k$ are selected to satisfy the equation:

$$Y=X+m_1+m_2+ \ldots +m_k$$

As shown in FIGS. **2**A and **2**B, the spinel compounds of the invention have low porosity and high density, especially compared to spinel compounds prepared from $MnCO_3$ (FIGS. **3**A and **3**B) and EMD (FIGS. **4**A and **4**B). In addition, FIG. **5** illustrates that the porosity of a spinel compound prepared according to the invention is significantly lower than the porosity of a spinel compound prepared from $MnCO_3$ as measured using Mercury porosimetry. In particular, FIG. **5** illustrates that the pore size and pore size distribution of a spinel compound prepared according to the invention is such that the pore volume of pores having a mean radius of less than 1 micron is about 10% of the pore volume of the spinel compound. The pore size and pore size distribution of a spinel compound prepared from $MnCO_3$, on the other hand, is such that the pore volume of the pores with a mean radius of less than 1 micron is about 45% of the total pore volume of the spinel compound. Because the volume of micropores (pores of less than 1 micron between the crystallites within the particles) is significantly less than the volume of macropores (pores of greater than 1 micron between the particles), the spinel compounds of the invention have a low porosity and thus have a high tap and pellet density compared, e.g., to spinel compounds prepared from $MnCO_3$.

Specifically, the spinel compounds of the invention have a tap density of greater than 1.9 g/cm^3, preferably greater than 2.1 g/cm^3. In addition, the spinel compounds of the invention preferably have a pellet density of greater than about 2.85 g/cm^3 and more preferably greater than 2.90 g/cm^3, or even greater than 2.95 g/cm^3. As is understood by those skilled in the art, the tap density is measured according to the method described in detail in the *Handbook of Manganese Dioxides* (1989) published by the International Battery Material Association. The pellet density is the measured density at 20,000 psi.

In addition to these properties, the porosity of the spinel compounds of the invention is such that the pore volume of the pores having a mean radius of less than 1 micron is no more than 20% and preferably no more than 15% or even no more than 10%, of the total pore volume of the spinel compound using Mercury porosimetry. These compounds also have a specific area of less than about 0.8 m^2/g, preferably less than about 0.6 m^2/g, or even less than about 0.5 m^2/g using a one point BET method. The mean particle size of the spinel compound of the invention is preferably between 7 μm and 30 μm. These compounds also are single phase compounds and preferably have a full width at half maximum of x-ray diffraction peaks from planes (400) and (440) using CuKα rays of less than about 0.15° 2θ, and more preferably less than or equal to 0.125° 2θ.

In addition to the advantageous physical characteristics of the spinel compounds of the invention, these compounds also exhibit superior electrical performance. Specific capacities and cycleabilities for these compounds are illustrated in FIGS. **6** and **7**.

In particular, these compounds have a capacity fade at room temperature between cycles 1–50 of preferably less than about 12%, and more preferably less than about 10%. Moreover, the capacity fade at room temperature for the compounds of the present invention between cycles 100–200 is preferably less than about 6%, more preferably less than about 5%.

The lithium manganese oxide spinel compounds of the invention possess the properties desired in the art including a desired metal oxide composition, structure, density and electrochemical performance. The spinel compounds prepared according to the present invention also have high tap and pellet densities. In addition, these spinel compounds have a predetermined mean particle size, particle size distribution, and high gravimetric specific energy. These spinel compounds can be used in the positive electrodes of secondary lithium and lithium ion cells to provide cells having high specific energy, safety cell performance, low manganese dissolution, low capacity fade during cycling and low capacity loss during storage at room and elevated temperatures.

It is understood that upon reading the above description of the present invention and reviewing the accompanying drawings, one skilled in the art could make changes and variations therefrom. These changes and variations are included in the spirit and scope of the following appended claims.

That which is claimed:

1. A highly crystalline Mn_2O_3 or Mn_3O_4 manganese oxide having a specific area of less than 2.0 m^2/g and a low porosity such that the pore volume of pores having a mean radius of less than 1 micron in said manganese oxide is no more than 20% of the total pore volume of said manganese oxide.

2. The manganese oxide of claim **1** wherein the specific area is less than 1.5 m^2/g.

3. The manganese oxide of claim **1** wherein the specific area is less than 1.0 m^2/g.

4. The manganese oxide of claim **1** further having a tap density of greater than 2.2 g/cm^3.

5. The manganese oxide of claim **1** further having a tap density of greater than 2.4 g/cm^3.

6. The manganese oxide of claim **1** having the formula Mn_2O_3.

7. The manganese oxide of claim **1** having the formula Mn_3O_4.

8. The manganese oxide of claim **1** formed by firing highly crystalline β-MnO_2 at a temperature greater than or equal to about 500° C. and less than or equal to about 1000° C.

9. The manganese oxide of claim **1** formed by firing highly crystalline β-MnO_2 at a temperature greater than or equal to about 600° C. and less than or equal to about 800° C.

10. The manganese oxide of claim **8** wherein the highly crystalline β-MnO_2 is formed by firing $Mn(NO_3)_2$ at a temperature greater than or equal to about 200° C. and less than about 400° C.

11. The manganese oxide of claim **8** wherein the β-MnO_2 has a mean particle size of greater than or equal to about 5 μm and less than or equal to about 20 μm.

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